interaction between the lone pair on the nitrogen with the metal d orbitals. Thus in the square-planar complexes, both the d_{xy} and the d_{xz} orbitals are raised in energy by the electrostatic interaction, leading to the nonzero values.

Summary

Ligand field electronic absorption transitions, including the d_{z^2} to $d_{x^2-y^2}$ transition and the spin-forbidden transitions, have been assigned in the low-temperature single-crystal polarized absorption spectra. The dipole-forbidden $^1A_2$ band shows the temperature dependence expected of a vibronic excitation. The angular overlap parameters show that NMe_3 is a strong σ donor and that its influence on the d orbitals of π symmetry through a proposed electrostatic interaction is significant.

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On the Observability of Cubic P_8

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A recent MNDO calculation predicts that the hypothetical P_8 is more stable than the observed gas-phase species P_4. The ab initio calculations reported here predict just the opposite but do establish that P_8 is more stable than another experimentally known form, P_2. The relative enthalpies (kcal/mol) are found to be as follows: $4P_2$, 72.4; $2P_4$, 0; P_8, 30.4. A force field analysis proves P_8 has a cubic structure. The bond length, vibrational frequencies, and photoelectron spectrum of P_8 are predicted.

Introduction

Just above its sublimation temperature of 704 K, phosphorus exists as tetrahedral P_4. Heating of the gas causes dissociation to diatomic molecules. These are the only two species identified at temperatures up to 1470 K.[1] Another possible allotrope, P_8, has never been conclusively identified.

P_8 is generally assumed to possess a cubic structure. The right angles in this configuration are close to the natural angles for phosphorus. For example, PH_3 has bond angles of 93.3°.[2] The relief of ring strain compared to $2P_4$ certainly makes cubic P_8 plausible.

A few polyphosphorus ionic species are known. P_8^{2+} has been claimed to be responsible for the blue color of solutions of phosphorus in disulfuric acid.[3] P_8^+ was detected by a mass spectrometer[4] in the vapor of subliming amorphous red phosphorus. This ion was present at 0.5% of the intensity of P_4^+, which would indicate that neutral P_8 was present in the vapor. A subsequent similar mass spectrometry experiment[5] failed to see any P_8^+, establishing an upper limit of 0.000 02 for the relative intensities of P_8^+ to P_4^+. (This later experiment did, however, detect As_8^+). A number of crystals containing the P_7^{3-} anion are known. The crystal structure[6] shows this anion consists of a nortricyclene structure. P_{16}^- consists of two such nortricyclene systems, joined by a bridging P_2 group,[7] rather than containing two P_8 units.

A recent communication by Halevi, Bock, and Roth[8] reported that the elemental modification P_8 is much more stable than two P_4 molecules, by 68 kcal/mol, according to MNDO calculations. However these authors speculated that P_8 is unobservable because the D_{3d} symmetry dimerization is Woodward–Hoffmann forbidden. Since alternative synthetic routes are certainly conceivable, their prediction of thermodynamic stability for P_8 is the main result and conflicts with two earlier ab initio studies.

The previous ab initio investigations of P_8 employed two different pseudopotential methods. Fluck, Pavlidou, and Janoschek[9] used an assumed bond length of 2.21 Å for both P_4 and P_8, and found P_8 to lie 47 kcal/mol above two P_4 molecules. Trinquier, Malrieu, and Daudey[10] did perform geometry optimization of the two species and found P_8 to lie 10 kcal/mol below two P_4. However, these authors stated that the incorporation of d orbitals in their calculations would probably reverse this conclusion.

The full weight of quantum chemistry has not yet been brought to bear on the $4P_2/2P_4/P_8$ system, because of its large size. For example, none of the previous theoretical investigations of P_8 used d orbitals on phosphorus. One of the calculations did not optimize the geometry. No one has checked the assumption that P_8 has a cubic structure. We describe here all electron ab initio calculations in extended basis sets that should help to resolve the current ambiguity concerning the relative energies of $2P_4$ and the as yet unobserved P_8. In addition, we report vibrational frequencies and ionization potentials for P_8 to assist in its experimental identification.

Theoretical Procedure

Geometry optimizations were performed on P_2, P_4, and P_8 with three types of basis sets. The minimal STO-2G and STO-3G bases[11] are used for comparison with the MNDO calculation,[8] since this is essentially a parameterized minimal basis calculation. As will be shown, the STO-NG bond lengths are reasonably good, especially compared to the very short MNDO bond lengths. The split-valence 3-21G basis[12] gives results comparable to those of the pseudopotential calculations,[10] including very long bond lengths. These long bond lengths are overcome by using the

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Table I. P_2 Results

method[a]	R(PP)[b]	energy[c]	HOMO[d]	LUMO[d]
STO-2G(0d)	1.9037	−655.151 07	−0.319	0.117
STO-3G(0d)	1.8955	−673.883 72	−0.335	0.099
3-21G(0d)	1.9293	−677.977 21	−0.380	0.007
3-21G(1d)	1.8533	−678.169 80	−0.378	0.030
6-31G(1d)	*e*	−681.424 50	−0.378	0.025
6-31G(2d)	*e*	−681.434 73	−0.375	0.032
MC(1d)	*e*	−681.465 84	−0.378	0.023
MC(2d)	*e*	−681.479 19	−0.376	0.027
spdf STO[f]	1.8510	−681.500 39		
MNDO	1.693[g]			
pseudo-sp	1.962[h]			
pseudo-spd	1.865[h]			
experiment	1.8934[i]			
MP2	*e*	−681.638 11		
MP3	*e*	−681.651 99		
MP4SDQ	*e*	−681.656 01		
MP4SDTQ	*e*	−681.669 29		

[a] Hartree–Fock level calculations, using the indicated basis set, or perturbation theory calculation at the indicated order, using the 6-31G(1d) basis set. [b] Bond length, in angstroms. [c] Total energy, in hartrees. (1 hartree = 627.5 kcal/mol). [d] Orbital energies, in hartrees. (1 hartree = 27.212 eV). [e] Computed at the 3-21G(1d) RHF bond distance. [f] Reference 24. [g] Reference 8. [h] Pseudopotential, with and without d orbitals, from ref 10. [i] Reference 32.

3-21G* basis,[13] which adds d orbitals on phosphorus, for geometry optimizations. The long 3-21G bond lengths are not due to inadequate treatment of ring strain in the present cyclic compounds but simply to the omission of d orbitals. For example, the 3-21G, 3-21G*, and experimental PP bond lengths for unstrained diphosphine are 2.356,[12] 2.205,[13] and 2.219 Å,[14] respectively. Similar conclusions about the need for d orbitals hold for the P═P double bond,[15,16] as well. The present paper will not follow the usual convention of asterisks to denote the use of d orbitals, but will use instead notation such as STO-2G(0d) for unaugmented STO-2G.

With reliable structures established at the 3-21G(1d) level, larger basis sets are used to establish accurate energetics. The 6-31G basis[17] is a larger split-valence basis and is complemented by one or two d functions. The McLean–Chandler basis[18] (abbreviated MC hereafter) is an extended basis set, of at least triple-ζ quality, and it is also augmented by one or two d functions. (Unfortunately the 8-bit index packing common to most quantum chemical programs precluded the use of two d orbitals with the MC basis for P_8.) When one d orbital is used with any of the sp bases, the exponent is 0.55.[17] Exponents of 0.22 and 0.77 are used for (2d) calculations. All calculations involving d orbitals retain the 3s contaminant of the Cartesian d functions.

Most of the results discussed here are taken from Hartree–Fock SCF level calculations, using the various bases described above. Electron correlation effects are not expected to contribute greatly to the reaction energy for $2P_4 \rightarrow P_8$, as both sides of this reaction have 12 PP σ bonds. Electron correlation may play a bigger role in reactions such as $4P_2 \rightarrow 2P_4$, since this reaction transforms π bonds to σ bonds. The importance of electron correlation was explored by Moller–Plesset perturbation theory calculations, carried to fourth order, including triples.[19] These calculations were done with the 6-31G (1d) basis only. Perturbation theory calculations on P_8 with realistic basis sets are beyond our current computational capabilities.

Geometry optimizations, vibrational analysis, and single-point energy calculations with extended bases were performed by using a locally modified version of GAMESS.[20] Perturbation theory computations were performed with GAUSSIAN82.[21]

Table II. P_4 Results[a]

method	R(PP)	energy	HOMO	LUMO
STO-2G(0d)	2.2508	−1310.437 35	−0.321	0.165
STO-3G(0d)	2.2595	−1347.858 94	−0.332	0.144
3-21G(0d)	2.4120	−1355.955 24	−0.362	0.032
3-21G(1d)	2.1627	−1356.390 74	−0.370	0.100
6-31G(1d)	*b*	−1362.899 74	−0.366	0.097
6-31G(2d)	*b*	−1362.927 43	−0.359	0.104
MC(1d)	*b*	−1362.983 26	−0.363	0.091
MC(2d)	*b*	−1363.016 79	−0.359	0.089
MNDO	2.052[c]			
pseudo-sp	2.370[d]			
pseudo-spd	2.190[d]			
experiment	2.2258[e]			
MP2	*b*	−1363.333 27		
MP3	*b*	−1363.355 14		
MP4SDQ	*b*	−1363.360 82		
MP4SDTQ	*b*	−1363.387 97		

[a] Columns have the same meaning as for Table I. [b] Computed at the 3-21G(1d) RHF bond distance. [c] Reference 8. [d] Reference 10. [e] Reference 22.

Table III. P_8 Results[a]

method	R(PP)	energy	HOMO	LUMO
STO-2G(0d)	2.2932	−2620.984 91	−0.272	0.100
STO-3G(0d)	2.3161	−2695.781 47	−0.289	0.079
3-21G(0d)	2.4361	−2711.961 82	−0.335	−0.049
3-21G(1d)	2.2649	−2712.738 51	−0.318	−0.011
6-31G(1d)	*b*	−2725.741 82	−0.315	−0.011
6-31G(2d)	*b*	−2725.799 90	−0.301	−0.0002
MC(1d)	*b*	−2725.917 68	−0.312	−0.011
MNDO	2.074[c]			
pseudo-sp	2.420[d]			

[a] Columns have the same meaning as for Table I. [b] Computed at the 3-21G(1d) RHF bond distance. [c] Reference 8. [d] Reference 10.

Results and Discussion

The computed geometries and energies for P_2, P_4, and P_8 are given in Tables I–III. For P_4, both STO-NG bases give bond lengths slightly longer than experiment, while 3-21G(1d) gives a bond length slightly shorter than experiment. The experimental bond length for P_4 is 2.223 Å, deduced from a Raman vibration–rotation band.[22] The often quoted value of 2.21 ± 0.02 Å is from an older electron diffraction experiment.[23] Omitting d functions from split-valence bases gives extremely long bonds. The 3-21G(0d) bond length of 2.41 Å is quite comparable to the 2.37-Å bond length reported previously,[10] which used a split-valence sp pseudopotential basis. For triply bound P_2, all bases give reasonable bond lengths, although even here 3-21G(0d) is somewhat long. Note that the MNDO calculations[8] gave bond lengths 0.15–0.20 Å shorter than experiment for both P_2 and P_4.

The best SCF energy computed for P_2 is nearly as low as that reached for extended Slater type basis sets.[24] P_4 has been the subject of several pseudopotential[9,10,25,26] and all electron[27–30] investigations. The total energies reported by the latter workers include −1362.0041 (no d's used),[28] −1361.94715 (with a d set),[29]

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Table IV. Vibrational Frequencies[a]

mode	calcd	scaled	exptl
P_2			
σ_g	998.7	773.2	780.77[b]
P_4			
e	452.3	350.1	360.8[c]
f_2	594.5	460.2	462.2[d]
a_1	801.1	620.2	606.5[d]
P_8			
e_u	248.7	192.5	
f_{2g}	337.4	261.2	
a_{2u}	454.2	351.6	
f_{1u}	546.7	423.2	
f_{2g}	558.2	432.1	
a_{1g}	563.7	436.3	
f_{2u}	591.3	457.8	
e_g	606.7	469.7	

[a] STO-2G vibrational frequencies, in cm^{-1}. Calculated frequencies are scaled by a factor 0.774. [b] Reference 32. [c] Reference 22. [d] Reference 33.

and −1360.71 (with a d set).[30] Table II shows that 6-31G(1d) and all higher level calculations reported here easily surpass the previous calculations.

The computed bond lengths for P_8 follow the same pattern as for P_4. 3-21G(0d) is clearly too long and is consistent with the earlier pseudopotential result. Once again, the MNDO calculations predict much too short a bond length. The STO-3G(0d) and the 3-21G(1d) bond lengths probably bracket the correct value (2.26–2.32 Å). If so, P_8 has bonds about 0.04–0.10 Å longer than does P_4.

The orbital energies included in Tables I–III showed that all bases larger than 3-21G(1d) predict about the same photoelectron spectrum. The rather unusual fact that the lowest unoccupied orbital of P_8 has a negative energy indicates that P_8 should have a large electron affinity. Since this orbital is of f_{1u} symmetry, this anion will undergo Jahn–Teller distortion. The full valence photoelectron spectrum of P_8 from the MC(1d) basis is as follows (in eV): 8.5, a_{1g}; 11.0, f_{1u}; 11.9, f_{2u}; 13.7, a_{1g}; 14.5, a_{2u}; 14.7, e_g; 19.9, f_{2g}; 24.5, f_{1u}; 28.5, a_{1g}. Most of these Koopmans' theorem ionization potentials differ by only a few tenths of an electronvolt from an earlier prediction,[10] except that the e_g and a_{2u} levels are shifted more than a volt and are reversed.

STO-2G force fields were calculated for all three molecules. The energy second derivatives were obtained by two-step finite differencing of analytic first derivatives. Since the resulting vibrational frequencies of P_8 are all real, the cubic structure represents a minimum energy conformation.

The results of the vibrational analyses of all three molecules are shown in Table IV. Hartree–Fock frequencies are normally larger than experimental values, particularly for minimal bases. Scaling the P_4 computed frequencies by 0.774 gives the best least-squares agreement with experimental values. Since the same scale factor gives good agreement with the experimental frequency for P_2, it is applied to P_8 as well. These scaled values are the predicted vibrational spectrum of P_8. The f_{1u} mode is IR-active, while the Raman-active bands are the a_{1g}, e_g, and two f_{2g} modes. From the scaled calculated frequencies, the harmonic zero-point energies of P_2, P_4, and P_8 are 2.2, 7.7, and 19.5 kcal/mol, respectively.

Relative energies for the various phosphorus species are shown in Table V. It is impossible to carry out a MC(2d) calculation on P_8 with our current programs. To estimate the MC(2d) relative energies we assume that the changes in energetics produced by adding a second d orbital set to the MC(1d) basis would be the same as adding a second d set to the 6-31G(1d) basis. As shown in Table V, this estimation compares quite well to the directly computed value for the reaction energy of $2P_2 \rightarrow P_4$. These reaction energetics have significant zero-point energy contributions, especially reactions involving the diatomic. Because of this the computed energy differences may not be directly comparable to experimental enthalpies at nonzero temperatures.

Table V. Reaction Energies[a]

	$2P_2 \rightarrow P_4$	$2P_4 \rightarrow P_8$	$4P_2 \rightarrow P_8$
STO-2G(0d)	−84.8	−69.2	−238.8
STO-3G(0d)	−57.4	−39.9	−154.7
3-21G(0d)	−0.5	−32.2	−33.3
3-21G(1d)	−32.1	27.0	−37.2
6-31G(1d)	−31.8	36.2	−27.5
6-31G(2d)	−36.4	34.5	−38.3
MC(1d)	−32.4	30.6	−34.1
MC(2d)	−36.7		
estd MC(2d)[b]	−37.0	28.9	−44.9
$\Delta H^\circ(298)$	−36.2	30.4	−42.4
experiment	−54.8 ± 1.0[c]		
MNDO[d]	−45	−68	−159
pseudo-sp[e]	3	−10	−4
pseudo-spd[e]	−30		

[a] In kcal/mol. [b] Estimated as described in text. [c] $\Delta H^\circ(298)$, ref 31. [d] Reference 8. [e] Reference 10.

We have used statistical mechanics to establish $\Delta H^\circ(298)$ enthalpy differences, accounting for translational, rotational, and vibrational degrees of freedom. Rotational moments of inertia were taken from the 3-21G(1d) structures, and the vibrational frequencies used were the scaled STO-2G values presented in Table IV. Standard approximations such as ideal gas, rigid rotation, and harmonic vibration were used. The resulting enthalpy differences are included in Table V. The $\Delta H^\circ(298)$ values differ only slightly from the electronic ΔE's.

The results show that P_8 is less stable than $2P_4$, but is more stable than $4P_2$. The data in Table V can be restated in terms of relative enthalpies for these 8P systems: $4P_2$, 72.4 kcal/mol; $2P_4$, 0 kcal/mol; P_8, 30.4 kcal/mol. P_8 is not as stable as $2P_4$, in spite of its advantage of ring strain relief. This may be due to its greater PP bond length, which, as described above, is found to be longer than in P_4.

The energy differences cited in the preceding paragraph are sufficiently different to imply the stability order is $2P_4 > P_8 > 4P_2$. However, the $\Delta H^\circ(298) = -36.2$ kcal/mol value computed for $2P_2 \rightarrow P_4$ deviates considerably from the experimental value of −54.8 kcal/mol.[31] The results in Table V show that calculations with split-valence basis sets predict about zero for this energy difference. Adding the first set of d orbitals gives about −32 kcal/mol, regardless of the particular sp basis used. Adding a second set of d orbitals gives a further improvement of 4–5 kcal/mol, which still leaves an error of about 18 kcal/mol.

In order to determine whether electron correlation effects account for this residual error, full fourth-order perturbation theory calculations were performed on P_2 and P_4. The energies of the various levels of perturbation theory are included in Tables I and II. The highest level, MP4SDTQ/6-31G(1d), gives an energy difference of −31.0, which is only 0.8 kcal/mol different from the SCF result with this basis. Reoptimization of the P_4 bond length at the MP4SDQ/6-31G(1d) level gives a slightly longer bond length, 2.20 Å, in very good agreement with experiment. However this reoptimization stabilizes P_4 by only 1.2 kcal/mol. The effect on the enthalpy difference will be even smaller, since P_2 would also be stabilized somewhat by geometry reoptimization. It may be that quantitative computation of the $2P_2 \rightarrow P_4$ enthalpy difference requires optimization of the d exponents, a set of f orbitals in the phosphorus basis, or an alternative treatment of the electron correlation.

Summary

The present work confirms that cubic P_8 is a reasonable synthetic target. It is not as stable as $2P_4$, but is more stable than

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the observed elemental modification $4P_2$. To assist in its experimental identification, we have predicted its geometry, vibrational frequencies, and photoelectron spectrum. P_8 should also have a large electron affinity.

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Note Added in Proof. Recent work by Raghavachari, Haddon, and Binkley[34] predicts the same order of stability $2P_4 > P_8 > 4P_2$ as our work. In addition, these workers established that the quantitative computation of the energy required for $P_4 \rightarrow 2P_2$ requires both a basis set containing f orbitals and at least third-order perturbation theory.

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Cryoscopy in the KCl–AlCl$_3$ System. High-Precision Phase Diagram near Equimolar Composition, with Comments on Oxide Contaminations and Effective Chloride Concentrations in Tetrachloroaluminate Melts

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The phase diagram of the KCl–AlCl$_3$ system near the equimolar composition is reported with high precision. The freezing point of the pure, congruently melting compound KAlCl$_4$ was determined to be 257.3 ± 0.1 °C. The molal freezing point depression constant of equimolar KCl–AlCl$_3$ melts was estimated to be 27 ± 2 °C kg mol^{-1}. The enthalpy of freezing for KAlCl$_4$ was found to be 18.0 ± 1.2 kJ mol^{-1}, in good agreement with the recently determined calorimetric value. The presence of oxide impurities in KCl–AlCl$_3$ melts was avoided by purifying the chemicals by fractionated recrystallization, and hence a phase diagram for melts essentially free of oxide impurities was obtained. The freezing point depression caused by deliberately added AlOCl showed dimerization, independent of the mole fraction in the range ~0.49 to ~0.52. Oxides dissolved in tetrachloroaluminate melts probably occur as $(AlOCl)_2(AlCl_4^-)_m$, $m = 1$ or 2, corresponding to solvation with one or two AlCl$_4^-$ species. The solubility has been cryoscopically determined to be ~0.08 and ~0.008 mol L^{-1} for NaCl and LiCl, respectively, in the KAlCl$_4$ melt at 257 °C, indicating $Na^+\cdots Cl^-$ and $Li^+\cdots Cl^-$ associations in this melt. The effective chloride concentration is approximately 10^2 times higher in KAlCl$_4$ than in NaAlCl$_4$ at the same mole fraction.

Introduction

Chloroaluminate melts have attracted considerable interest as general-purpose high-temperature ionic solvents, with low crystallization temperatures.

Previously, we considered the phase diagram of the NaCl–AlCl$_3$ system and found that it was inaccurately known in the vicinity of the equimolar mixture.[1]

The present work is a continuation study dedicated to the analogous KCl–AlCl$_3$ system. Detailed measurement of the phase diagram near the equimolar composition is reported, as is the molar freezing point depression constant for KAlCl$_4$ and its enthalpy and entropy of fusion. Further, the problem of oxide contaminations in tetrachloroaluminate melts is discussed.

Experimental Section

Chemicals. Because of the cryoscopic effect of impurities, very highly purified chemicals are needed for the determination of an accurate phase diagram. KCl (analytical reagent from Merck, >99.5% by weight) was purified (in a quartz apparatus) by first passing HCl gas over the solid and then through the melt (at ca. 850 °C), flushing with pure N$_2$, and finally filtering the melt. AlCl$_3$ was made and purified by distillation followed by recrystallization. LiCl, NaCl, CsCl, and CsBr of >99.5% purity were used after being dried at 150 °C for 2 days. AlOCl of >98.5% purity was prepared as previously described.[1] Especially purified KAlCl$_4$ was prepared by several fractionated recrystallizations, starting from a mixture of KCl and AlCl$_3$ with a slight excess of AlCl$_3$. After six recrystallizations the melting point remained constant at 257.30 ± 0.05 °C.

Technique. To prevent hydration of the chemicals, all manipulations were performed quickly in a dry N$_2$ glovebox. Chemicals were constantly stored under vacuum in sealed glass containers. Grinding to powders was avoided to keep moisture uptake at the lowest possible level. These precautions were necessary to obtain reproducible results.

Cryoscopic cells, the furnace, and other experimental details were described previously.[1] All temperatures were measured with the same 100-Ω platinum resistance thermometer system, which was calibrated to an absolute accuracy of ±0.1 °C (reproducibility on the order of 0.03 °C), by using ice water and 99.999 wt % pure Sn and Zn (231.97 and 419.58 °C).[2] The measured freezing points remained stable even after the melts were tempered for weeks.

Compositions are expressed in mole fractions, e.g. X_{AlCl_3} = mol of AlCl$_3$/(mol of AlCl$_3$ + mol of KCl). Oxides are not included in the mole fractions. Melts with X_{AlCl_3} >0.5, <0.5, and =0.5 are referred to as acidic, basic, and neutral, respectively.

Results and Discussion

KCl–AlCl$_3$ Phase Diagram. Before we report our own results, it is worth briefly mentioning previous results. The available information[3-11] is collected in Figure 1, which shows the consid-

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